Journal of Industrial and Engineering Chemistry 17 (2011) 445–449

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Synthesis of novel triphenylene-based discotic liquid crystals with naphthalene moiety in the side chains for photo-polymerisation

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ARTICLE INFO

Article history:
Received 11 January 2011
Accepted 22 February 2011
Available online 28 April 2011

Keywords:
Discotic molecule
Triphenylene
Naphtalene
Photo-polymerisation

ABSTRACT

Rod-like naphthalene and the molecule 4,-(7,-(4,-(triphenylene-2,3,6,7,10,11-hexaylhexakis(oxy))hexakis(butane-4,1-diyl))hexakis(oxy)hexakis(naphthalene-7,2-diyl))hexakis(oxy)hexakis(butane-4,1-diyl) hexaacrylate, to which an acryloyl group that enabls photo-polymerisation is introduced, are synthesised nearby discotic triphenylene. Differential scanning calorimetry shows that a liquid crystalline form is observed at 69 °C. In XRD measurements, a new peak appears at $2\theta = 22$, indicating partial nematic liquid crystalline properties. As a result of photo-polymerisation, successful polymerisation of over 70% is verified through FT-IR. UV–vis spectroscopy was used to measure the transmittance of the polymerised film, demonstrating a high transmittance level of over 94%.

1. Introduction

Since discotic liquid crystals (DLCs) were first reported in 1977 by the Chandrasekhar group, and many liquid crystalline substances with discotic properties have been synthesised and reported [1,2]. With recent dramatic developments in research on DLCs, roughly 3300 new compounds have been studied and reported [3–5]. These substances are either flat or nearly flat due to the aliphatic core chain situated nearby. Discotic substances generally show one of the following two types of mesophases: nematic and columnar. A discotic nematic phase refers to a modified arrangement made in a single direction overall without any regular intervals; in a discotic columnar phase, molecules undergo stacking on a regular basis, forming another columnar phase overall. Demonstrating such wide-ranging crystalline phases, rod like polymers including DLCs have been used in numerous device applications such as organic photovoltaics [6–8], one-dimensional conductors [9,10], and light-emitting diodes [11,12]. A few groups have synthesised a discotic triphenylene derivative with a conductor containing a functional side chain to use the resulting compound in applications [13,14].

Since the discotic nematic (N_d) phase was first discovered in 1981 from 2,3,6,7,10,11-hexayl hexakis(4-n-alkoxy benzoate) derivatives, and numerous studies have been carried out in relation to this. The discotic nematic liquid crystal materials exist in both rod and disc types, reducing the generation of the smectic phase in the discotic molecule and forming a nematic phase overall [15,16].

A substance showing this N_d phase was recently used to produce a film with negative birefringence, and commercial success was achieved on this basis for the first time. Fuji Photo Film Company produced films through photo-polymerisation of a triphenylene-based discotic nematic liquid crystal material and successfully developed compensation films for a LCD with a wide-view angle [17,18].

Based upon this background, we synthesised a new triphenylene-based discotic molecule with a naphthalene derivative as its side chain. The triphenylene derivative has excellent thermal and chemical stability; the naphthalene derivative was used to create a different version of birefringence from triphenylene with discotic properties and to generate an N_d phase overall. An alkenyloxy group was introduced to control the phase transition as a surrounding spacer, and an acryloyl group was adopted to induce effective photo-polymerisation. The liquid crystalline properties of the synthesised conductor were evaluated using ^{1}H NMR, differential scanning calorimetry (DSC), UV–vis spectroscopy, X-ray diffraction, and Fourier transform spectroscopy (FT-IR).

2. Experiment

2.1. Materials and measurement

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures.

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1226-086X/$ – see front matter © 2011 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jiec.2011.02.042

All column chromatographies were performed with the use of silica gel (230–400 mesh, Merck) as the stationary phase. ^1H NMR spectra were recorded with a Bruker ARX 400 spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. Chemical shifts were recorded in ppm units. DSC measurements were carried out at a heating and cooling rate of 2 °C/min using a TA Instruments Model 2310 modulated DSC. Electronic absorption spectra were measured in chloroform using a HP Agilent 8453 UV–vis spectrophotometer. FTIR spectra were recorded with Mattson instruments Genesis FTIR^{TM} spectrometer. X-ray powder diffraction analysis (XRD, Rigaku, D/Max 2200) using CuKα was conducted to identify the product phase. Cyclic voltammetry experiments were performed with a Zahner IM6eX Potentionstat/Galvanostat. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a nonaqueous Ag/AgCl reference electrode at the scan rate of 50 mV/s. The solvent in all experiments was acetonitrile and the supporting electrolyte was 0.1 M tetrabutyl ammonium-tetrafluoroborate.

2.2. Synthesis of monomers

2.2.1. 2,7-bis(4-bromobutoxy)naphthalene (1)

2,7-dihydroxynaphthalene (25 g, 156.08 mmol), 1,4-dibromobutane (101.09 g, 468.24 mmol), and potassium carbonate (64.71 g, 468.24 mmol) were dissolved in acetone (500 ml) and the mixture was refluxed for 24 h under in nitrogen. The solvent of reaction mixture was removed under reduced pressure. After washing with water, ethanol was added to remove excess 1,4-dibromobutane and which was filtered. The precipitate was purified by silica gel column chromatography using $CHCl_3$ as the eluent. Yield 30.26 g (45%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1–3 (8H, CH_2), 4–5 (4H, OCH_2), 4–5(4H, $BrCH_2$), 7–8 (6H, ArH).

2.2.2. 4,4′-(naphthalene-2,7-diylbis(oxy))dibutan-1-ol (2)

Aqueous 50% dioxane (1000 ml) was added to a stirred mixture of compound **1** (30.26 g, 70.34 mmol) and CaCO3 (105.60 g, 1.05 mol), and the mixture was heated at a reflux for 3 days. After the solvent was evaporated, the residue was dissolved in aqueous 6 M HCl (300 ml) and the precipitate was collected by filtration. Then the crude product was dissolved in EtOH and filtered. The solvent was removed under reduced pressure. This product was used without further purification. Yield 19.78 g (92%) ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1–3 (8H, CH_2), 1–3 (2H, OH), 4–5 (8H, OCH_2), 7–8 (6H, ArH).

2.2.3. 4-(7-(4-bromobutoxy)naphthalen-2-yloxy)butan-1-ol (3)

PPh_3 (17.05 g, 65.01 mmol) dissolved in THF was added to a stirred mixture of compound **2** (19.78 g, 65.01 mmol) and CBr_4 (21.49 g, 65.01 mmol) in THF. The solvent of the reaction mixture was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (EA/MC 1:9) Yield: 7.77 g (32%) ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1–3 (8H, CH_2), 1–3 (1H, OH) 4–5 (6H, OCH_2), 4–5(2H, $BrCH_2$), 7–8 (6H, ArH).

2.2.4. 4-(7-(4-bromobutoxy)naphthalen-2-yloxy)butyl acrylate (4)

To a dichloromethane solution of compound **3** (6.20 g, 16.88 mmol) and TEA (3.41 g, 33.76 mmol), a MC solution of acryloyl chloride (3.05 g, 33.76 mmol) was added dropwise. The reaction mixture was stirred at 0 °C and allowed to increase to room temperature within 24 h. The solvent of the reaction mixture was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using MC solution as the eluent. Yield: 6.04 g (85%) ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1–3 (8H, CH_2), 4–5 (6H, OCH_2), 4–5(2H, $BrCH_2$), 6–7 (3H, $CHCH_2$), 7–8 (6H, ArH).

2.2.5. 2,3,6,7,10,11-[hexaylhexakis(oxy))hexakis(butane-4,1-diyl))hexakis(oxy)hexakis(naph-thaene-7,2-diyl))hexakis(oxy)hexakis(butane-4,1-diyl)hexaacrylate]triphenylene (5)

Compound **4** (2.97 g, 7.06 mmol), 2,3,6,7,10,11-hexahydroxy triphenylene (0.19 g, 0.58 mmol), and potassium carbonate (2.0 g, 14.47 mmol) were dissolved in DMF (20 ml), and the reaction mixture was stirred at 70 °C for 24 h under nitrogen. Ethyl acetate was added to the reaction mixture, and the organic phase was washed with water and brine. After drying over sodium sulphate, ethyl acetate was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (EA/MC 4:6). Yield: 1.08 g (78%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1–3 (48H, CH_2), 4–5 (48H, OCH_2), 6–7 (18H, $CHCH_2$), 7–8 (42H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$, δ, ppm): 166.25, 157.44, 148.91, 135.91, 130.70, 129.10, 128.48, 124.12, 123. 65, 116.22, 107.06, 106.11, 105.92, 77.32, 77.07, 76.81, 69.17, 67.45, 67.15, 64.22, 26.17, 25.85, 25.48.

2.3. Photopolymerisation

Compound **5** was spin-coated onto TAC film and photopolymerised using UV light. It was comprised of an 81 wt% product, 10 wt% trimethylol propane triacrylate, 4.5 wt% Igaqure907, and 4.5 wt% 1,4-butanediol diacrylate. Propylene glycol monomethyl ether acetate was used as a solvent, with the content of solid vs. solvent set at 20 wt%. Spin-coating was performed at 1000 rpm to a thickness of 1.2 µm. UV hardening was carried out with a Philips HPA 400/30S lamp for 10 min.

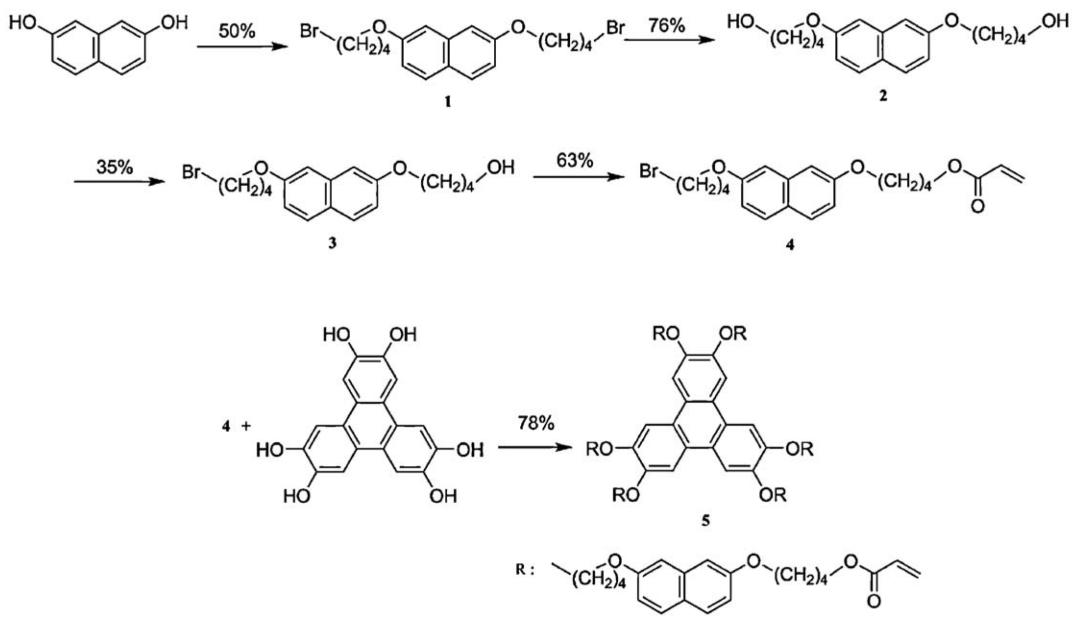
3. Results and discussion

We synthesised a discotic molecule using the synthesis pathway illustrated in Scheme 1, which utilises a simple method to facilitate synthesis. Compound **1** was synthesised through the reaction of 2,7-dihydroxynaphtalene and 1,6-dibromohexane using potassium carbonate as the base. Compound **2** was synthesised through reduction reactions using calcium carbonate. For compound **3**, bromination was performed on only one side using carbon tetrabromide with triphenyphosphine as a catalyst. For compound **4**, an acryloyl derivative with triethylamine as the base was synthesised. Lastly, compound **5** was synthesised based on The Williamson ether synthesis (the same as Monomer 1) using potassium carbonate as the base. The average yield for the entire synthesis process was approximately 60%.

As for the final, post-synthesis structure of compound **5**, we applied proton NMR to evaluate whether the synthesis was successfully achieved, as illustrated in Fig. 1. A new peak that had not previously been observed was found at 7.8 ppm for the existing compound **4**, which was shown to be the peak of the triphenylene derivative. The peak corresponding to the Br–H of compound **4** disappeared in the NMR of compound **5** and shifted downfield to 4.3 ppm to generate another new peak. This demonstrates that the synthesis was successful in six sites.

We analysed changes in the phase transition temperature and enthalpy using DSC. Scanning was performed at a rate of 2 °C/min, and the DSC measurement results are described in Fig. 2. Phase transition was not observed during the heating process; the DSC samples turned into liquid crystals at 58 °C and showed no phase transition at all during freezing.

The phase assignment of compound **5** was verified using X-ray diffraction. A powder sample of compound **5** was used for measurement and produced different X-ray diffraction patterns accordance to temperature, as shown in Fig. 3. A new broad peak appeared after heating at 100 °C and then cooling to room temperature. This indicates partial ordering between triphenylene cores, implying that the discotic molecule shows a N_d phase.



Scheme 1. . Synthesis of the triphenylene derivative.

The sample was dissolved in chloroform to measure the transmittance spectrum in the forms of solution and film, and the results are shown in Fig. 4. The solution shows an average transmittance level of 99%, and the film demonstrates a high average transmittance level of 95%, suggesting its suitability for the production of a compensation film, optical spacer, and other devices that require high transmittance. Fig. 5 described the HOMO and LUMO levels acquired using the onset values of cyclicvoltammetry. The HOMO value was calculated by the formula below after compensation using ferrocene.

$$\text{HOMO (eV)} = -4.8 - (E_{\text{onset}} - E_{1/2}(\text{ferrocene}))$$

As a result, the HOMO level of compound **5** was 5.66 eV, the LUMO level in cyclicvoltammetry was barely observable. Accord-

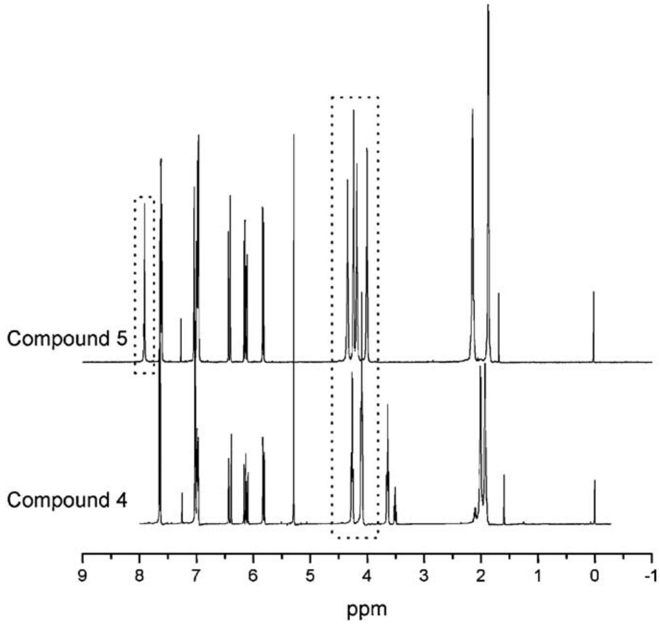


Fig. 1. ^{1}H NMR spectrum of compound **5**.

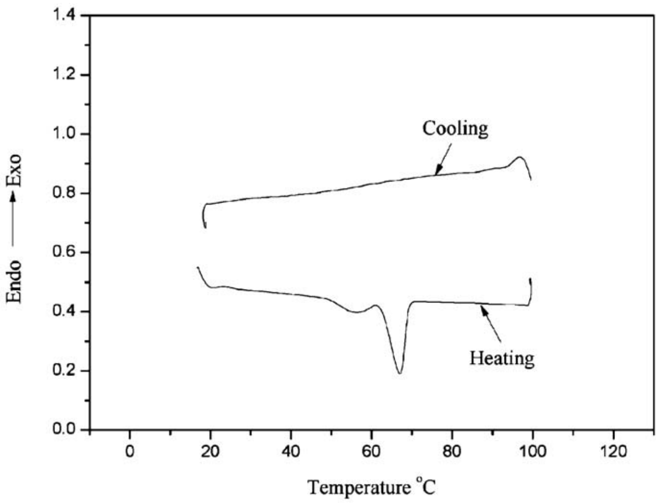


Fig. 2. DSC heating and cooling traces of compound **5**.

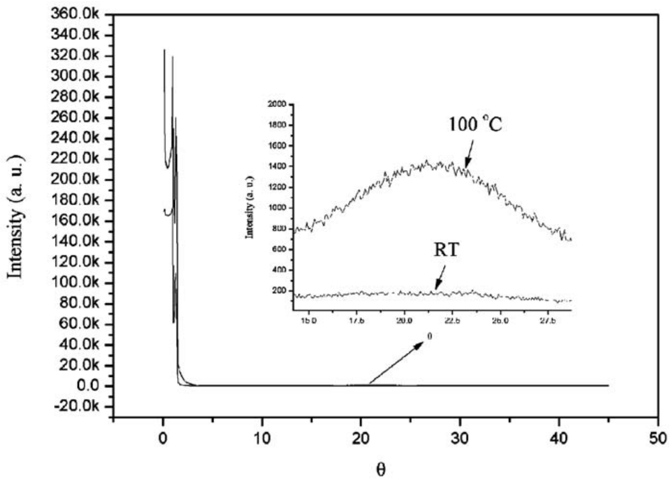


Fig. 3. X-ray diffraction patterns of compound **5** at (A) RT and (B) 100 °C.

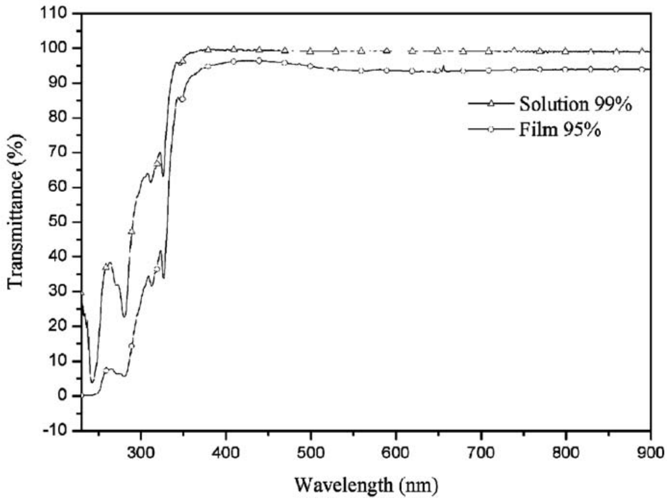


Fig. 4. Transmittance spectroscopy of compound **5**.

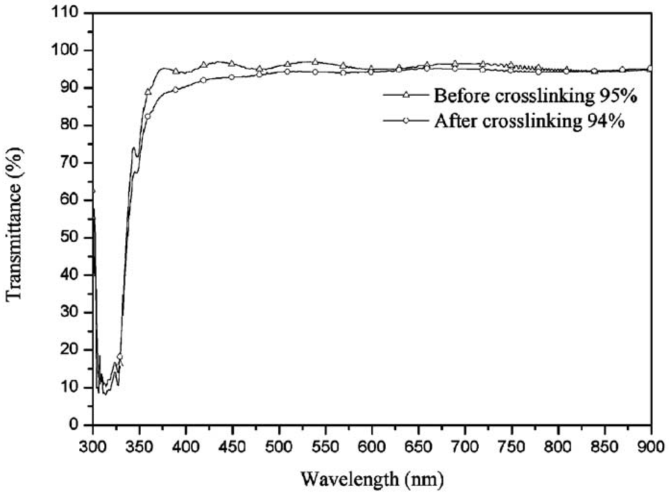


Fig. 7. Transmittance spectroscopy of the crosslinked polymer.

ingly, the LUMO level was calculated from the difference between the HOMO energy levels and the optical band-gap, which was 1.97 eV, suggesting its possibilities for the production of electron blocking and hole injection layer of OLED.

The synthesised monomer was spin-coated onto TAC film and photo-polymerised using UV light. The results of photo-polymerisation were verified with FT-IR, as illustrated in Fig. 6. The FT-IR results show that the peaks at 1636, 1411, and 1294 cm^{-1} (the characteristic peaks of the acryloyl group) were significantly lowered, implying that photo-polymerisation was successfully performed by about 70%. The results of transmittance measurements were obtained using the UV–vis spectrophotometer and are shown in Fig. 7. The transmittance level of the post photo-polymerisation product declined slightly compared to before photo-polymerisation, but the overall level was similar, with a high transmittance level of 94%, which is suggesting its suitability for the production of a compensation film, other devices that

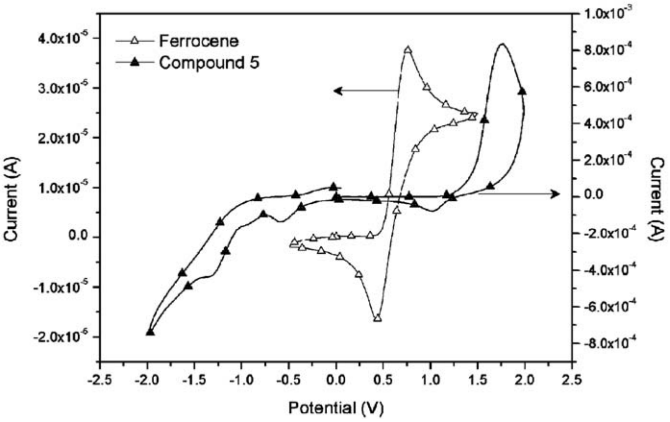


Fig. 5. Cyclic voltammograms of compound **5**.

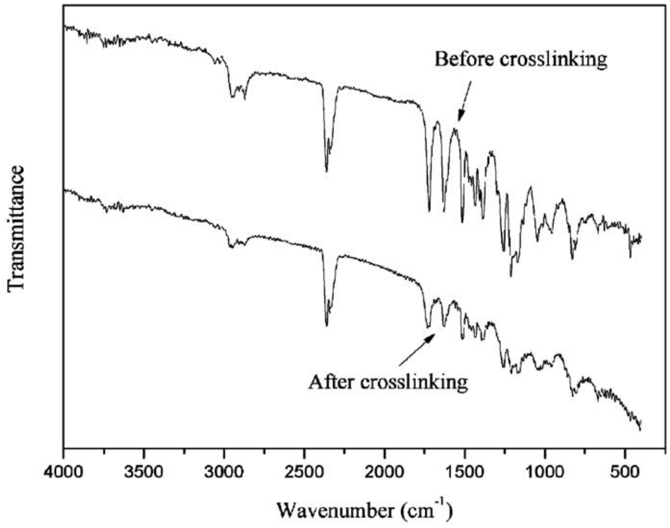


Fig. 6. FT-IR transmittance spectroscopy of the crosslinked polymer.

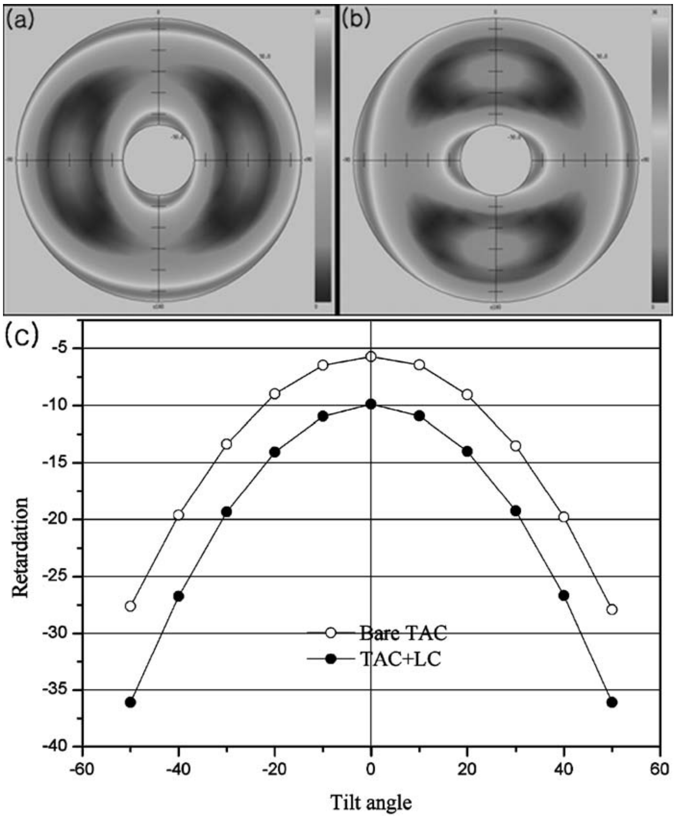


Fig. 8. (a) bare TAC film; (b) TAC film coating compound **5**; (c) retardation value of bare TAC film and TAC film coating compound **5** measured from different measuring angle.

require high transmittance. The results of retardation values were obtained using the UV–vis spectrophotometer and are shown in Fig. 8. The retardation value of the post photo-polymerisation TAC film showed retardation difference of 10 nm compared to bare TAC film. Thus, it is suggesting its suitability for VA mode required property of negative C plate in LCD industry.

4. Conclusions

In conclusion, a disc-shaped molecule, linked with an alkyl chain spacer to a discotic triphenylene core and nematic naphthalene derivative, was successfully synthesised. Although the molecule has a discotic form overall, it combines both nematic and discotic units and was shown to have a nematic mesophase. It is suggesting molecules suitable for the production of a compensation film, optical spacer, blocking layer, other devices that require high transmittance.

Acknowledgments

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea and this work was supported by the Konkuk University.

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